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## (54) ELECTRODE MATERIAL FOR METAL-HALOGEN SECONDARY BATTERY

(57)Abstract:
PURPOSE: To provide an electrode material capable of maintaining high discharge potential even at low bromine concentration plus high current density toward the end of discharge at the positive electrode of a metal-halogen secondary battery, esp. zinc-bromine battery (i.e., bromine electrode).

CONSTITUTION: An electrode prepared by jointing to an electrically conductive plate a paperlike material containing fibrous activated carbon ≥1.0% in the proportion of the number of the nitrogen atoms on the surface to that of the carbon atoms and ≥2.0meq/g in the amount of acidic groups per weight, is used as the positive electrode of a metal-halogen secondary battery. Use of this electrode can maintain the polarization at a low level even at low bromine concentrations, thereby, maintaining high discharge potential even at high current density toward the end of discharge.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the electrode material and electrode which are used for the positive electrode, i.e., the zinc pole, of a metal-halogen rechargeable battery, especially a zinc-bromine rechargeable battery.
[0002]
[Description of the Prior Art] A metal-halogen rechargeable battery, for example, a zinc-bromine rechargeable battery, discharges by returning a bromine to bromine ion in a positive electrode. It is demanded that a positive electrode, i.e., a bromine pole, makes the reduction reaction of the bromine at the time of the discharge which affects the energy efficiency of a cell react quickly and effectively in this rechargeable battery. Although platinum has been conventionally used as a positive-electrode electrode material, since it is expensive, the electroconductive-plastics plate and carbon sintering plate which carried out hot forming of the mixture of conductive powder carbon and resin are used. However, since depression of potential would become remarkable if discharge progresses in these electrodes and the concentration of the bromine which is positive active material falls, the energy efficiency of charge and discharge was low. The fall of potential was so remarkable that especially current density became high.
[0003] In order to make [ many ] an electrode surface product and to take many reaction area with a bromine as an approach of solving this problem, said electroconductive-plastics plate is used as an electrode substrate, and activated carbon is joined to a front face, or it scours to an electrode substrate, and is crowded and used for it. Moreover, the example which uses [ the example ] the textiles of porous carbon fiber and knitting fabric-like cloth for JP,59-29385,A to an electrode substrate, joining is proposed. Moreover, there is an example which joins and uses fibrous paper-like activated carbon, in the Provisional-Publication-No. sum No. 163765 [ 59 to ], fibrous activated carbon with large pore volume is made into the shape of paper very much, and the thing whose pore [ the 30-1000A pore of fibrous activated carbon ], i.e., pore diameter, pore volume is 0.1 or more cc/g and which is used joining to an electrode substrate is proposed.
[0004]
[Problem(s) to be Solved by the Invention] Although the above-mentioned fibrous activated carbon is applicable to an electrode material as textile fabrics, knitting fabric, and a papyraceous material, joining especially a papyraceous material to an electrode substrate, and using it as a positive electrode attracts attention also from lowering the price of a cell in recent years. However, at the time of discharge, if the concentration of the bromine which is positive active material falls, the so-called polarization to which depression of potential becomes remarkable will arise, and the energy efficiency of charge and discharge will be reduced. Polarization is so remarkable that especially current density becomes high.
[0005] this invention person came to offer the electrode material and electrode of a metal-halogen rechargeable battery from which polarization is low and high discharge potential is obtained also with high current density also by low bromine concentration, as a result of examining wholeheartedly

adsorbent [ which contribute to a reaction / the front face of fibrous activated carbon and adsorbent / of a bromine ] in view of this situation.
[0006]
[Means for Solving the Problem] This invention is an electrode for metal-halogen rechargeable batteries with which a surface joint nitrogen atomic number is characterized by joining the electrode material for sheet-like metal-halogen rechargeable batteries and this electrode material containing the fibrous activated carbon whose amount of acidic groups per 1.0% or more and unit weight is 2.0 or more meq/g to a conductive plate to a carbon atomic number. The detail of this invention is explained below.
[0007] the fibrous activated carbon used in this invention -- organic fiber -- carbonization -- activation is carried out and it is obtained. Although the organic fiber used as a raw material has a cellulose system, a phenol novolak system, a polyacrylonitrile system, an aromatic polyamide system, a polyvinyl alcohol system, a polyvinyl chloride system, petroleum, or a coal pitch system, if it can become fibrous activated carbon, it will not be limited to these. Generally as carbonization and the approach of activation, a well-known approach can be used. Moreover, depending on the case, activation may be carried out using a well-known activation catalyst.
[0008] The acidic group in this invention means the hydroxyl group (- OH) of a fibrous activated carbon front face, a carboxyl group (-COOH), the hydroxy amino group (-NH-OH), and a hydroxyimino group (=N-OH). The amount of the acidic group of the fibrous activated carbon used for this invention is 2.0 or more meq/g per unit weight of fibrous activated carbon, and its thing of 2.5 or more meq/g and 5.0 meq/g or less is desirably good. The wettability of fibrous activated carbon and the electrolytic solution improves by this, and the front face of fibrous activated carbon is used effectively. However, when the fibrous activated carbon of less than 2.0 meq/g per unit weight is used, the wettability of fibrous activated carbon and the electrolytic solution gets worse, since the area with which a reaction is presented substantially decreases, a bromine cannot be adsorbed effectively, but polarization increases.
[0009] Moreover, the front joint nitrogen atomic number in this invention means the nitrogen volume of the fibrous activated carbon front face detected by ESCA surface analysis (the analysis approach is mentioned later), and it expresses as a rate to the carbon atomic number of a surface joint nitrogen atomic number (it is called a following N/C ratio%). Although an unpaired electron is formed on a front face of nitrogen atom installation of the front face of fibrous activated carbon, reactivity with the strong bromine of an electron affinity is puffed up with this unpaired electron. Therefore, it can be made hard to happen polarization, in order for reactivity with the bromine of the fibrous activated carbon with which a N/C ratio presents electrode reaction 1.0% or more by using 15% or less of fibrous activated carbon 1.5% or more desirably to improve and to make a low-concentration bromine react efficiently. However, when it is less than 1.5%, reactivity with a bromine gets worse quickly, and since it is hard coming to adsorb a bromine, polarization increases.
[0010] The fibrous activated carbon with many amounts of acidic groups used by above-mentioned **** this invention is obtained by oxidizing so that the organic fiber of said publication may be made into weight yield under the oxygen ambient atmosphere which has the oxygen tension of 0.01 or more torrs after carrying out activation, carbonization and and it may become 30 - 99% of range. If weight yield becomes less than 30%, surface etching will advance, the rise of contact resistance is imitated, and it is not desirable at that of **. Moreover, there are oxidation in a nitric-acid water solution and the approach of making generate the plasma using a RF under the ambient atmosphere containing oxygen, and oxidizing in the plasma as other oxidation approaches of fibrous activated carbon. A predetermined acidic group can be obtained also in these approaches, and you may carry out combining these approaches.
[0011] It is desirable when obtaining organic fiber, such as the raw material containing a nitrogen atom, for example, a polyacrylonitrile system, and an aromatic polyamide system, carbonization and by carrying out activation especially as an approach of furthermore introducing nitrogen into fibrous activated carbon where a simple substance or other organic fiber is mixed considers a manufacturing cost. However, after introducing the amino group into a front face by after [ oxidation in the gas phase ] hydrazine processing as mentioned above or acid-chloride-izing the fibrous activated carbon obtained

with the raw material which does not contain the usual nitrogen atom by the thionyl chloride, a nitrogen atom may be introduced into a front face like a chemical treatment of introducing an amide group using various amines. moreover, a raw material -- the bottom of an ammonia ambient atmosphere -- carbonization -- or activation may be carried out.

[0012] Thus, although especially the specific surface area of the chosen fibrous activated carbon does not prepare a limit, it should just be 500-2000m2/g obtained by the well-known manufacture approach.

[0013] The created fibrous activated carbon like **** is fabricated in the shape of a sheet. The shape of a sheet is textiles, knitting, or a papyraceous material. In order to obtain reinforcement especially fixed in paper formation, paper making is carried out so that the amount of eyes may set it two or more 25 g/m and thickness may be set to 0.15mm or more with others, organic [ one or more kinds of ], and an inorganic material. In addition, if especially reinforcement is not needed, it will not be limited to this. In addition, although especially the content of the fibrous activated carbon in a papyraceous material does not prepare a limit, it is desirable that it is 60 % of the weight or more.

[0014] As long as it is required as other ingredients used for fibrous activated carbon and coincidence as a papyraceous material besides pulp and the aggregate, starch and various additives other than a binder like polyvinyl alcohol, such as a ** agent, a surfactant, a release agent, a defoaming agent, and a flocculant, may be added. The pulp used may use the other natural pulp of the pulp of a regenerated-cellulose system, acrylic, and a polyamide system, although the synthetic pulp of the polyethylene which is excellent in a water resisting property and chemical resistance, and polypropylene is desirable. Although chopped fiber and these stratified fiber (sheath core fiber) of the polyethylene which is excellent in a water resisting property and chemical resistance as the aggregate, and polypropylene are desirable, a straight chain and/or an aromatic polyamide system, polyester, a phenol novolak, a glass fiber besides the organic fiber of a polyacrylonitrile system, asbestos, a quartz, and the various inorganic fibers of an alumina can be used. These pulp and the aggregate are not limited to the material indicated by point ** that what is necessary is just that from which fixed reinforcement is obtained after paper formation.

[0015] The conductive plate as used in the field of this invention is the electrode substrate which carried out hot forming of the mixture of conductive impalpable powder-like carbon and resin. The junction to an electrode substrate and an electrode material The conductive matter which made carbon, such as carbon black and a carbon fiber, the subject so that it may become 30 % of the weight or more It mixes with polyethylene resin powder to homogeneity, and after covering so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], it is stuck to what carried out the heat press and was produced as a 1.0mm [ in thickness ], and magnitude 10cm square conductive electrode substrate by pressure under pressurization and heating.

[0016] Next, the measuring method of the amount of acidic groups used in this invention, specific surface area, a N/C ratio, and the polarization value of an electrode is described.

(1) The amount of acidic groups : it dried, after fully rinsing the fibrous activated carbon containing an acidic group, about 1g was extracted, at 120 degrees C, the vacuum drying was carried out for 12 hours, weighing capacity was carried out, and it was immersed in the 60ml NaOH water solution [ 1/N / 10 ], and shook at 25 degrees C for 10 hours. This liquid was filtered with the sintered glass filter, the filtrate was isolated preparatively to 25ml accuracy, and the back titration was carried out with the 1/N [ 10 ] HCl standard solution. On the occasion of titration, the phenolphthalein was used as an indicator. The blank test was performed similarly and the amount of acidic groups per unit weight of fibrous activated carbon was calculated by several 1.

[0017]

For the inside D of a formula, the normality of the 1/N [ 10 ] HCl standard solution and W of the amount (ml) and K which subtracted the titration value in a blank test from the titration value of the 1/N [ 10 ] HCl standard solution are the weight (g) of fibrous activated carbon.
[0018] (2) Specific surface area : about 0.1g of fibrous activated carbon was extracted, at 120 degrees C, it dried for 12 hours, weighing capacity was carried out, several phase counter pressure was gradually measured for the amount of adsorption of the nitrogen gas in the boiling point (-195.8 degrees C) of liquid nitrogen with slight height in 0.0 to 0.2, and it asked for the specific surface area per unit weight (m2/g) by B.E.T plot.
[0019] (3) N/C ratio : measure the N/C ratio of the fibrous activated carbon front face made to fully dry by the X-ray photoelectron spectroscopy currently called ESCA or XPS for short. The measuring device used ESCAPAC760 for Shimazu ESCA 750 and analysis. Electrode material was started to 6mmphi and it stuck on the heating sample base with a conductive paste, and it measured, after carrying out a vacuum deairing for 3 hours or more, heating a sample at 120 degrees C. To the line source, the degree of vacuum in equipment analyzed the sample front face on condition that 10-7torr using MgK alpha rays (1253. six eV). In addition, the front face said here means the depth field from the outermost layer of a sample to dozens of A. Measurement is performed to C1S and N1S peak, and it asks for each peak area using ESCAPAC760. Obtained area was **(ed) [ S / C1] with the relative intensity of 1.77 about 1.00 and N1S based on the correction method by J.H.Scofield, and the direct surface (nitrogen/carbon) atomic ratio was computed by % from the value.
[0020] (4) The polarization value of an electrode : evaluate the electrode of this invention of point ** as a positive electrode, i.e., a bromine pole of a zinc-bromine cell, using the equipment which shows discharge potential to drawing 1 R> 1. The electrolytic solution dissolved the bromine into the three mols [/l. ] zinc bromide solution, and measured the current density cm of 60mA/square and bromine concentration at the time of discharge by l. in 0.1 mols /. In addition, current density is based on a geometric area of an electrode. Using 99.99% of rolling zinc plate for the counter electrode, measurement temperature used the saturated calomel electrode as 25 degrees C and a reference pole. It is Vi about the potential of the halogen pole when setting open circuit potential of the halogen pole in predetermined bromine concentration to Vopen, and passing the current of a predetermined consistency. It carries out and they are Vopen and Vi. The difference was made into the polarization value. It is so good that the above-mentioned part extremal value is small as a halogen pole of a metal-halogen rechargeable battery.
[0021]
[Example] Although this invention is explained with an example below, it is not limited to this.
(Example 1) 2.0d of single fiber sizes and polyacrylonitrile fiber with a die length of 54mm were used as the raw material, and after heating for 30 minutes and fire-resistance-izing at 260 degrees C among air, the nonwoven fabric of 400g[/m ] 2 eyes was manufactured. Then, it carbonized by carrying out a temperature up over about 90 minutes to 1000 degrees C under a nitrogen air current, and holding 1000 degrees C for 60 minutes. For back 60 minutes which furthermore lowered temperature to 850 degrees C, it cooled radiationally, after performing steam activation processing, and it heat-treated for 10 minutes at 500 degrees C among air further. In this way, the amount of acidic groups of the obtained fibrous activated carbon was [ the specific surface area of 2.9 meq/g and a N/C ratio ] 763m2/g 13.1%. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 38g/m2, and a papyraceous material with a thickness of 0.21mm were created.
[0022] Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject 1.0mm in thickness, and magnitude 10cm square of carbon was created. The papyraceous material of

point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was in 83mV.

[0023] (Example 2) 2.0d of single fiber sizes and polyacrylonitrile fiber with a die length of 54mm were used as the raw material, and after heating for 30 minutes and fire-resistance-izing at 260 degrees C among air, the nonwoven fabric of 400g[/m ] 2 eyes was manufactured. Then, it carbonized by carrying out a temperature up over about 90 minutes to 1100 degrees C under a nitrogen air current, and holding 1100 degrees C for 60 minutes. For back 90 minutes which furthermore lowered temperature to 850 degrees C, it cooled radiationally, after performing steam activation processing, and it heat-treated for 10 minutes at 500 degrees C among air further. In this way, the amount of acidic groups of the obtained fibrous activated carbon was [ the specific surface area of 2.7 meq/g and a N/C ratio ] 592m2/g 7.0%. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 41g/m2, and a papyraceous material with a thickness of 0.24mm were created. Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject 1.0mm in thickness, and magnitude 10cm square of carbon was created. The papyraceous material of point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was 75mV.

[0024] (Example 3) 2.0d of single fiber sizes and polyacrylonitrile fiber with a die length of 54mm were used as the raw material, and after heating for 30 minutes and fire-resistance-izing at 260 degrees C among air, the nonwoven fabric of 400g[/m ] 2 eyes was manufactured. Then, it carbonized by carrying out a temperature up over about 90 minutes to 1200 degrees C under a nitrogen air current, and holding 1200 degrees C for 60 minutes. For back 90 minutes which furthermore lowered temperature to 950 degrees C, it cooled radiationally, after performing steam activation processing, and it heat-treated for 10 minutes at 600 degrees C among air further. In this way, the amount of acidic groups of the obtained fibrous activated carbon was [ the specific surface area of 2.8 meq/g and a N/C ratio ] 544m2/g 3.6%. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 43g/m2, and a papyraceous material with a thickness of 0.26mm were created. Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject 1.0mm in thickness, and magnitude 10cm square of carbon was created. The papyraceous material of point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was 92mV.

[0025] (Example 4) 5.5d of single fiber sizes and regenerated-cellulose fiber with a die length of 76mm were used as the raw material, the nonwoven fabric of 600 g/m2 eyes was manufactured, and dibasic calcium phosphate was infiltrated 10% to fiber weight by drying a dibasic-calcium-phosphate water solution after immersion and a diaphragm to these nonwoven fabrics. This was heated at the inside of inert gas, and 270 degrees C for 30 minutes, furthermore, the temperature up was continuously carried out over about 90 minutes from 270 degrees C to 850 degrees C, and for 800 degrees C and 60 minutes, steam activation processing was performed and it heat-treated for 9 minutes at 500 degrees C among air further. It rinsed and dried, after processing this at 95 degrees C furthermore for 1 hour among the 10-%

of the weight water solution of hydroxylamine 2 hydrochloride. In this way, the amount of acidic groups of the obtained fibrous activated carbon was [ the specific surface area of 2.7 meq/g and a N/C ratio ] 966m2/g 6.3%. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 39g/m2, and a papyraceous material with a thickness of 0.22mm were created. Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject 1.0mm in thickness, and magnitude 10cm square of carbon was created. The papyraceous material of point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was 96mV.

[0026] (Example 5) The nonwoven fabric (the Unitika, Ltd. make, Type A-10) of the pitch system fibrous activated carbon marketed was heat-treated for 10 minutes at 500 degrees C among air. It rinsed and dried, after processing this at 95 degrees C furthermore for 3 hours among the 10-% of the weight water solution of hydroxylamine 2 hydrochloride. In this way, the amount of acidic groups of the obtained fibrous activated carbon was 2.6 meq/g, the N/C ratio was 2.0%, and specific surface area was 1078m2/g. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 39g/m2, and a papyraceous material with a thickness of 0.25mm were created. Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject 1.0mm in thickness, and magnitude 10cm square of carbon was created. The papyraceous material of point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was 118mV.

[0027] (Example 6) 2.0d of single fiber sizes and phenol novolak fiber with a die length of 62mm were used as the raw material, and the nonwoven fabric of 300 g/m2 eyes was manufactured, and the temperature up of this nonwoven fabric was carried out over about 90 minutes among inert gas to 850 degrees C, and it carbonized, and for 800 degrees C and 60 minutes, steam activation processing was performed and it heat-treated for 10 minutes at 500 degrees C among after [ cooling ] air. It rinsed and dried, after processing this at 95 degrees C furthermore for 2 hours among the 10-% of the weight water solution of hydroxylamine 2 hydrochloride. In this way, the amount of acidic groups of the obtained fibrous activated carbon was 2.8 meq/g, the N/C ratio was 2.5%, and specific surface area was 889m2/g. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 42g/m2, and a papyraceous material with a thickness of 0.22mm were created. Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject 1.0mm in thickness, and magnitude 10cm square of carbon was created. The papyraceous material of point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was 91mV.

[0028] (Example 1 of a comparison) 5.5d of single fiber sizes and regenerated-cellulose fiber with a die length of 76mm were used as the raw material, the nonwoven fabric of 600 g/m2 eyes was manufactured, and dibasic calcium phosphate was infiltrated 10% to fiber weight by drying a dibasic-calcium-phosphate water solution after immersion and a diaphragm to these nonwoven fabrics. This was heated at the inside of inert gas, and 270 degrees C for 30 minutes, furthermore, the temperature up was continuously carried out over about 90 minutes from 270 degrees C to 850 degrees C, and for 800 degrees C and 60 minutes, steam activation processing was performed and it heat-treated for 10 minutes at 500 degrees C among air further. In this way, the amount of acidic groups of the obtained fibrous activated carbon was [ the specific surface area of 2.9 meq/g and a N/C ratio ] 1020m2/g 0.5%. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 40g/m2, and a papyraceous material with a thickness of 0.25mm were created. Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject with 1.0mm in thickness and a 10m magnitude [ 2 square ] carbon was created. The papyraceous material of point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was 150mV.

[0029] (Example 2 of a comparison) 2.0d of single fiber sizes and polyacrylonitrile fiber with a die length of 54mm were used as the raw material, and after heating for 30 minutes and fire-resistance-izing at 260 degrees C among air, the nonwoven fabric of 400g[/m ] 2 eyes was manufactured. Then, it carbonized by carrying out a temperature up over about 90 minutes to 1100 degrees C under a nitrogen air current, and holding 1100 degrees C for 60 minutes. For back 90 minutes which furthermore lowered temperature to 850 degrees C, it cooled radiationally, after performing steam activation processing. In this way, the amount of acidic groups of the obtained fibrous activated carbon was [ the specific surface area of 0.2 meq/g and a N/C ratio ] 584m2/g 7.0%. After grinding this fibrous activated carbon by the cutter mill, this was made into dry weight, and was extracted by 80 % of the weight, the binder of 12% of the weight of polypropylene single fiber chopped fiber, 6% of the weight of the synthetic pulp made from polyethylene, and 2% of the weight of polyvinyl alcohol was added to this, and the amount of eyes of 41g/m2, and a papyraceous material with a thickness of 0.25mm were created. Moreover, after covering with what mixed conductive carbon powder with polyethylene resin powder to homogeneity so that it might become 30 % of the weight so that it may become the thickness more fixed than resin softening temperature at the bottom of the metal mold set up more highly [ 10 degree-C ], the conductive electrode substrate which carried out the heat press and made the subject 1.0mm in thickness, and magnitude 10cm square of carbon was created. The papyraceous material of point ** was stuck to this electrode substrate by pressure under pressurization and heating, and the electrode of a metal-halogen rechargeable battery was obtained. Thus, the polarization value of the obtained electrode was 325mV.

[0030]

[Effect of the Invention] Since contact nature of the electrode material of this invention with the electrolytic solution improves by giving many amounts of acidic groups per unit weight of the fibrous activated carbon used, and its compatibility with the bromine which is an active material improves by installation of the nitrogen atom of a fibrous activated carbon front face further and it adsorbs a bromine effectively as explained above, also in high current density, the small electrode of polarization can be offered by low bromine concentration.

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[Translation done.]